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THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS AT THE MICROGRAM/1 LEVEL IN WATER BY GAS CHROMATOGRAPHY

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November 1974

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16. ABSTRACT

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By

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Methods Development and Quality

Assurance Research Laboratory

Program Element No. 1BA027

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report describes the development of a new method for quantitative recovery and determination of volatile organic compounds in water and waste water. The method provides for the determination of compounds such as organohalide solvents, e.g., chloroform, and others having low water solubility at levels that heretofore could not be measured. Using this method, many organic compounds can be detected at 0.5 µg/l and below. The development of this method has opened up a whole new area for research. Using the method, toxicologists will be able to measure and study the potential chronic toxic or carcinogenic effects of low concentrations of selected organic compounds in water.

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ABSTRACT

A quantitative analytical method for the concentration, isolation, and determination of volatile hydrocarbon and chlorinated hydrocarbon solvents in water is presented. An inert gas is bubbled through the sample to transfer volatile compounds from the aqueous phase to the gaseous phase. These compounds are then concentrated on a porous polymer trap under non-cryogenic conditions and determined by gas chromatography using a flame ionization or microcoulometric detector. Details of the design, fabrication, and use of the apparatus are described.

The method is applicable to organic compounds that are less than 2% soluble in water and that boil below 150°C. Application of the method to the determination of a variety of aliphatic and aromatic hydrocarbons has been demonstrated on several types of water including sewage treatment plant effluents. The lower limit of detection is 0.5 to 1 µg/l for many compounds. The method is useful over a concentration range of approximately 1 µg/l to 2500 µg/l.

CONCLUSIONS

The method presented here provides for the gas chromatographic determination of volatile organic compounds that are less than 2% soluble in water and that boil below 150°C. It has been found applicable to the determination of substituted and unsubstituted aliphatic and aromatic hydrocarbons. Selective determination of organohalogen compounds is possible using a microcoulometric detector. The method is equally applicable to finished waters, natural surface and ground waters, and sewage treatment plant and industrial effluents. The useful concentration range for quantitative analysis is approximately 1 µg/l to 2500 µg/l. The lower limit of detection for many compounds is 0.5 to 1 µg/l.

INTRODUCTION

Recent legislation (1-2) requires analytical methods for the determination of hydrocarbon and chlorinated organic solvents in waste water. In some cases a minimum detectable limit of 1 µg/l is required for specific compounds. It is the responsibility of the Methods Development and Quality Assurance Research Laboratory to evaluate existing methods and when necessary to develop new methods to meet such needs. Determination of these substances at the 1 µg/l level has been difficult. Commonly used techniques such as direct aqueous-injection gas chromatography, liquid/liquid extraction, and head gas analysis have proven inadequate. Direct aqueous-injection gas chromatography (3-4) although generally useful for analysis of industrial effluents, provides an approximate limit of detection of only 1000 µg/l. Liquid/liquid extraction methods using low (5) or high (6) boiling organic solvents followed by gas chromatographic analyses have been investigated. These methods have provided erratic or low extraction efficiencies for volatile compounds. In addition, large solvent responses and solvent impurities can cause serious chromatographic interferences. Distillation techniques (7) have been employed in which a small quantity of sample distillate is collected and analyzed by direct aqueous injection gas chromatography. Detection limits of approximately 1 µg/l have been reported for water soluble volatiles using this method. Poor recoveries render the method useless for water insoluble components. Head gas techniques (8) have been routinely employed for a number of years. With this method the sample is sealed in a partially filled container. Each volatile organic compound establishes an equilibrium between the gaseous and aqueous phase. At low concentrations the ratio of the concentration in the gaseous phase to the concentration in the aqueous phase is a constant (partition coefficient) and is unique for each organic compound. By analyzing the gaseous phase and applying the appropriate partition coefficient the concentration can be calculated for each organic originally present in the aqueous phase.

Of the techniques mentioned above, the head gas method has the greatest potential for meeting the needs set forth in the Federal Register. For this method to be effective, the following must be accomplished.

1. Transfer of 95% to 100% of the organics contained in the aqueous phase into the gaseous phase.

2. Quantitative injection of all of the organics contained in the gaseous phase into a gas chromatography.

If these can be done, 5.0 ml of aqueous sample would be sufficient to provide a method sensitive to 1.0 µg/l; this sample size is based upon the average limit of detection for direct aqueous injection techniques.

Since, in a static system, it is impossible to alter the partition coefficient to favor the gaseous phase 100%, it was decided to study a dynamic system where a sweep (purge) gas is bubbled through the sample until the volatile organics are quantitatively transferred to the gaseous phase. The organics that are quantitatively transferred to the gaseous phase could then be concentrated for gas chromatographic analysis with the use of a non-cryogenic trapping technique developed a number of years ago for ambient air (9) and dilute emission analysis (10). In this manner an analysis performed upon the gas phase would have a direct relationship to the aqueous phase concentration.

EXPERIMENTAL

Apparatus

Several pieces of commercial equipment are modified and assembled to meet the needs of the method. A list of parts required and instructions for assembling the purging device, trap, and desorbers are given in the Appendix.

Purging Device - This specially designed glassware (Figure 1) allows finely devided gas bubbles to pass through the sample. Volatile, water insoluble compounds boiling less than 150°C are transferred from the aqueous phase to the gaseous phase in a quantitative manner using less than 300 ml of purge gas.

Trap - The trap (Figure 2) is a short section of stainless steel tubing packed with an adsorptive material such as gas chromatographic grade porous polymers, silica gel, or molecular sieve. Volatile materials are transported directly from the purging device into the trap by the purge gas. The adsorbant retards the flow of the purged compounds while the purge gas is vented. The properties of the adsorptive material are chosen to meet the needs of the particular analysis. The following criteria must be met:

> The volume of the purge gas passing through the adsorbant packed in the trap can approach but not reach the retention volume of the compound to be trapped.
>
> The retained compounds must not be irreversibly sorbed by the trap. [Silica gel irreversibly adsorbs some aromatics above C_9 (9).]
>
> No chemical reactions or rearrangements may take place as the sample is being concentrated, stored, or desorbed. [Silica gel causes externally bonded olefins to rearrange to the cis- and trans-2 olefins (9).]
>
> The adsorptive material must be thermally stable. Chromosorb 103 and Tenax GC have been found to perform satisfactorily. [Divinyl benzene crossliked porous polymers out-gas extraneous compounds causing serious interferences during most gas chromatographic analyses (10).]

Desorbers - The desorbers (Figures 3 and 4) are used to transfer the contents

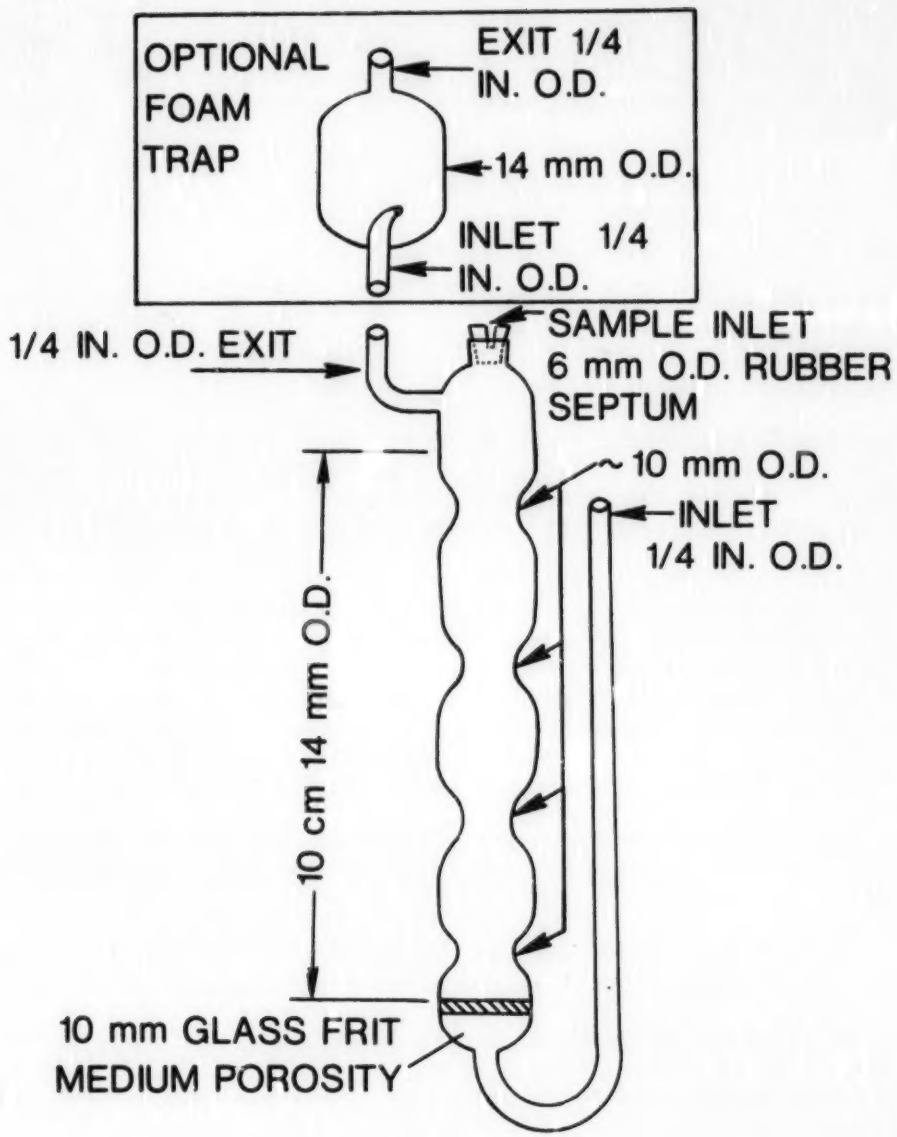

FIGURE 1. PURGING DEVICE

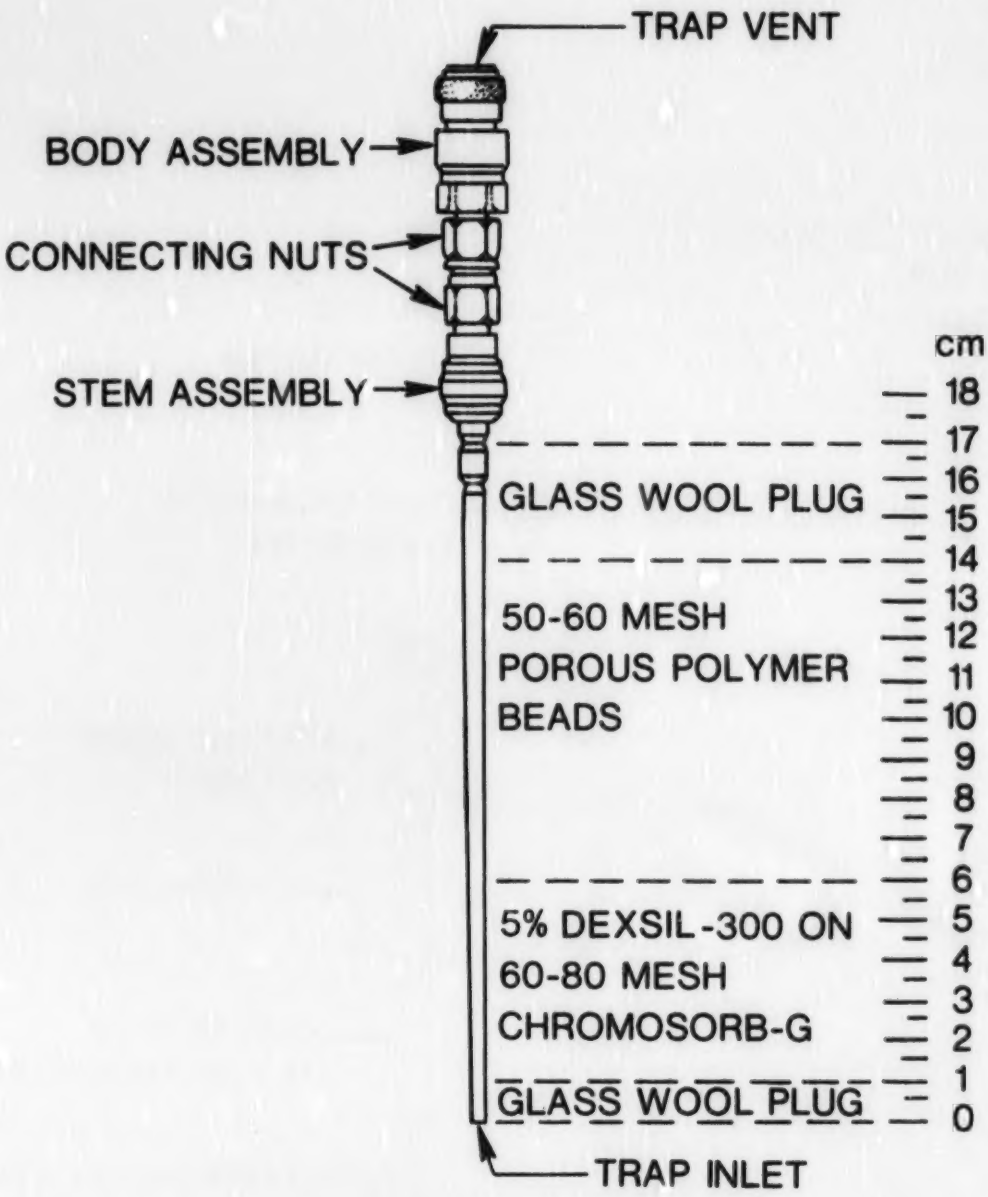

FIGURE 2. TRAP

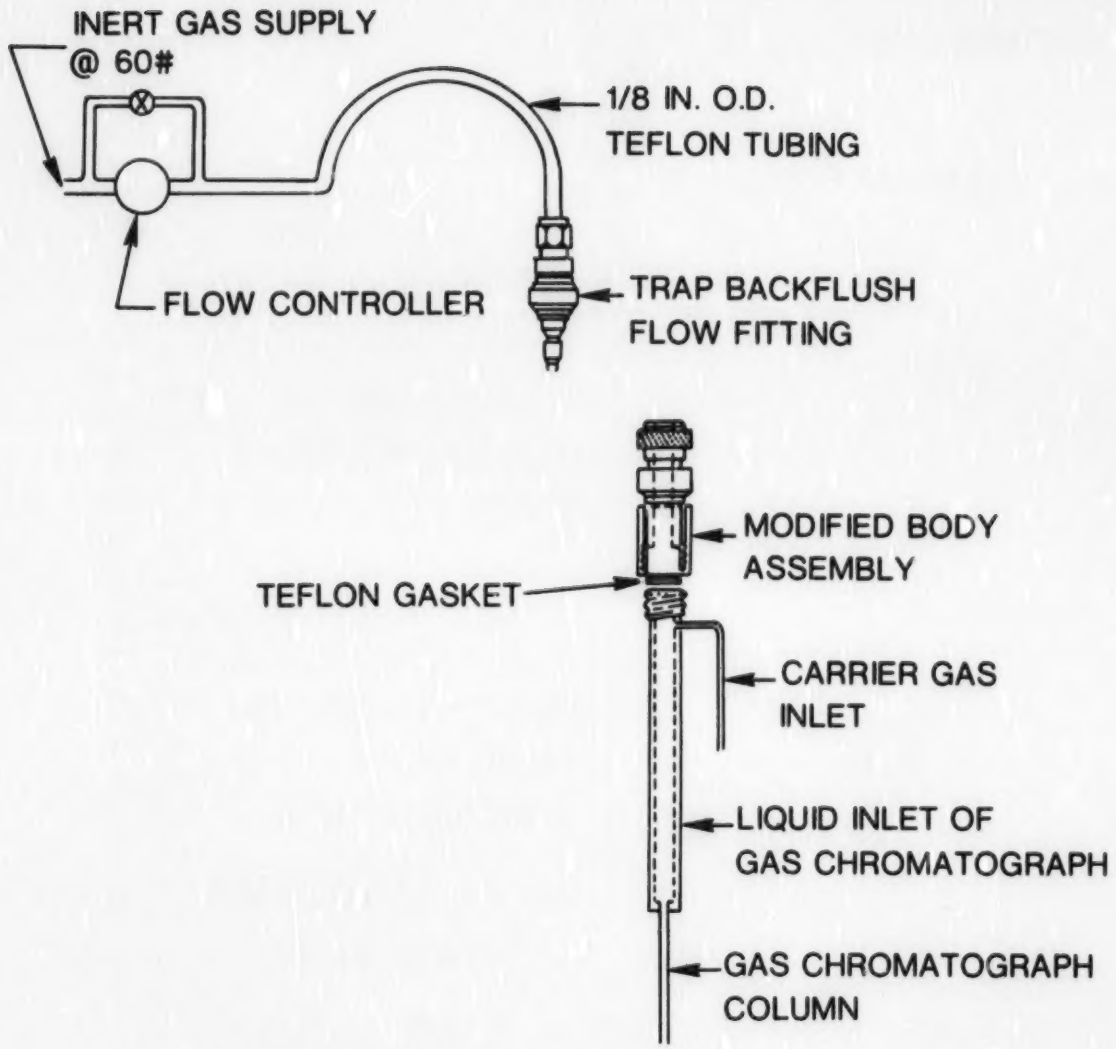

FIGURE 3. DESORBER #1

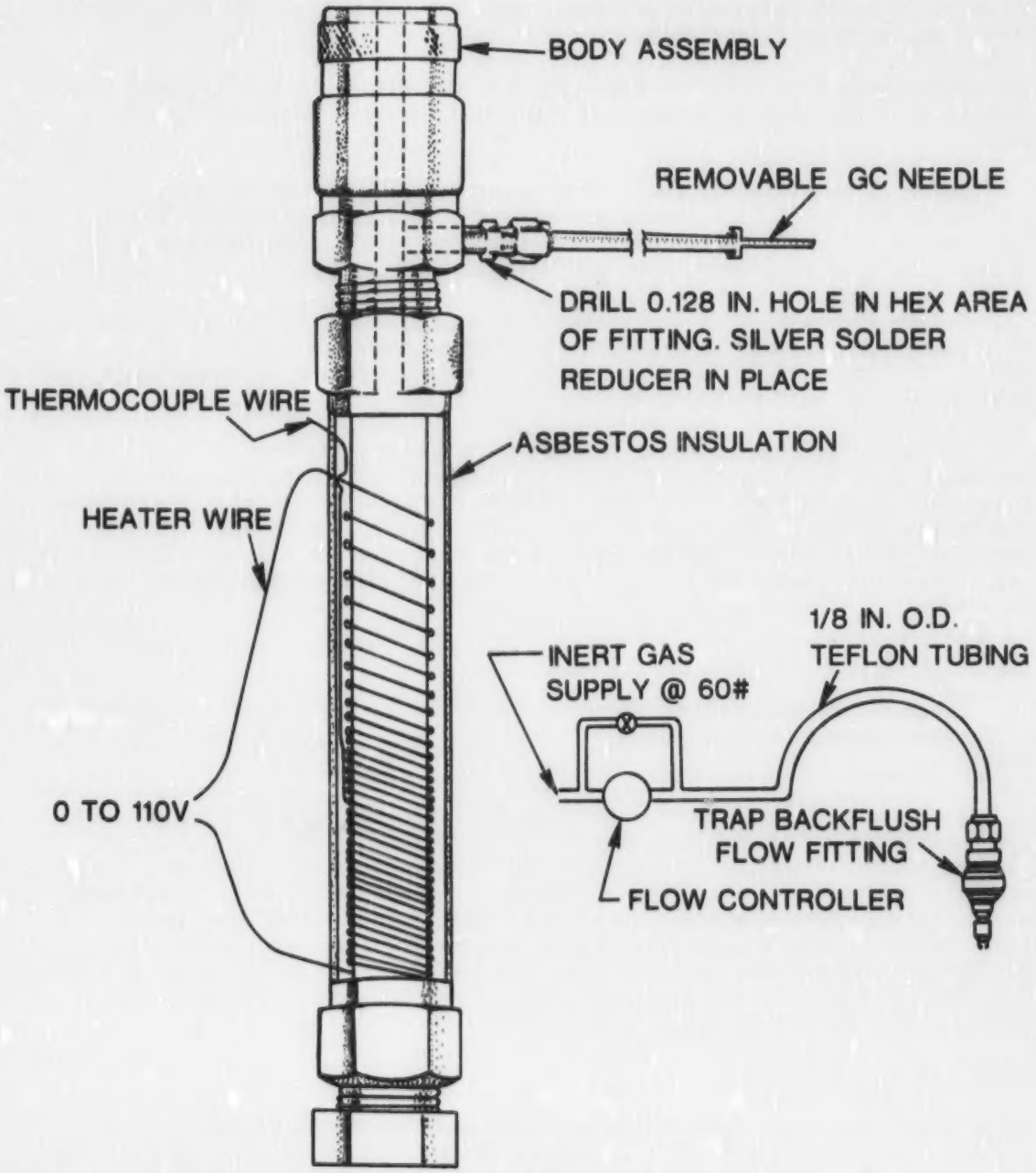

FIGURE 4 DESORBER #2

of the trap to the gas chromatograph for analysis. This is done with the use of an auxilliary carrier flow control system that backflushes the trap at elevated temperatures directly onto the gas chromatographic column. Desorber #1 is used exclusively with a Perkin-Elmer 900 series gas chromatograph and desorber #2 can be used as a universal desorber for all gas chromatographs with a septum-type liquid inlet system.

Gas Chromatograph - A Perkin-Elmer 900 Gas Chromatograph was equipped with dual-flame ionization detectors and a microcoulometric detector (halide mode).

Column 1 consisted of dual, stainless-steel, 180 cm (6 ft) long x 2.67 mm (0.105 in) I.D. columns, packed with Chromosorb-101 (60/80 mesh). The carrier gas was nitrogen at 50 ml/min. The oven temperature was isothermal 190°C or programmed from 120°C to 225°C at 10°/min.

Column 2 consisted of dual, stainless-steel, 91 cm (3 ft) x 1.65 mm (0.065 in) I.D. columns packed with 4% SE-30 on Chromosorb-P(NAW) (60/80 mesh). The carrier gas was nitrogen at 50 ml/min. The oven temperature was programmed from 60°C to 230°C at 10°/min.

The gas chromatograph-mass spectrometer system consisted of a Varian Aerograph Series 1400 with a Finnigan 1015C Quadrupole Mass Spectrometer controlled by a Systems Industries 150 Data Acquisition System. The column was glass, 240 cm (8 ft) long x 2 mm (0.078 in) I.D. and packed with Chromosorb-101 (50/60 mesh). The carrier gas was helium at 30 ml/min. The initial oven temperature was held at 125°C for 3 min, and then programmed at 4°C/min to 220°C.

Reagents

Organic-free Water, water free of interfering organics, was prepared by passing distilled water through a Millipore Super-Q water treatment system.

Standard stock solutions were prepared by injecting 1 to 5 µl of the compound to be determined into a 1-liter volumetric flask partially filled with organic-free water. The mixture was then diluted to volume with organic-free water to give concentrations between 1 and 7 mg/l. Dilutions were then made from the stock solution by pipetting a known quantity of stock solution into a partially filled volumetric flask and diluting to volume with organic-free water. [For low level work (1 to 10 µg/l), a 1:10 dilution of the stock solution was prepared and secondary dilutions were prepared from this solution as required.]

Procedure

Purging and Trapping - Samples were purged and trapped as follows: With nitrogen gas flowing through the purging device (Figure 1) at 20 ml/min, the trap inlet (Figure 2) was attached (finger-tight) directly to the purging device exit using a compression fitting. The trap vent was inserted into the exit end of the trap. Five milliliters of sample was injected into the

purging device and purged for the specified time (11 min). The trap was then removed from the purging device and the vent plug was removed and replaced with a cap to seal the trap inlet.

Trap Conditioning. Newly packed traps were conditioned at approximately 200°C with a nitrogen flow of 20 ml/minute for 16 to 24 hr with one of the desorbers and vented tc the room. Each day before use, traps were placed into the desorber and conditioned at 130°C for approximately 10 min while being backflushed with nitrogen at 20 ml/min.

Desorption and Analysis - Two desorbers were designed for desorption and analysis. One was designed exclusively for use with the Perkin-Elmer model gas chromatograph and the other was designed for use with any gas chromatograph.

Desorber #1 (Figure 3). The gas chromatographic oven was cooled to below 30°C with the oven door open. The "plug" was removed from the desorber and the cap was removed from the trap. The trap was then inserted into the desorber and locked into place. The trap backflush flow fitting was then locked into place on the trap exit flow fitting and backflushed with nitrogen at 20 ml/min for 3 min between 125° and 130°C. The trap backflush flow fitting was removed (trap still locked in place), the oven lid closed, and the oven rapidly heated to its normal or initial operating temperature. Gas chromatographic analysis was carried out under these conditions.

After analysis, the trap was removed by: 1) inserting the trap vent into the trap exit fitting (to vent inlet system), 2) removing the trap, 3) resealing GC inlet system with "the plug", 4) removing the trap vent, and 5) resealing the trap inlet with the cap.

Desorber #2 (Figure 4). The gas chromatographic oven was cooled to below 30°C. The needle was inserted into the liquid inlet system on the gas chromatograph. The trap was then inserted into the desorber and locked into place. The trap backflush flow fitting was locked into the trap exit flow fitting and backflushed with nitrogen at 20 ml/min for 3 min between 125° and 130°C. After desorption and sample transfer was completed, the needle was removed from the liquid inlet system, the oven lid closed, and the oven repidly heated to the normal or initial operating temperature. Gas chromatographic analyses were performed under these conditions. After sample transfer the trap was removed and sealed for future use.

Investigation of Method Parameters

Initial studies were carried out to determine the volume of purge gas needed for quantitatively extracting selected volatile materials from a water sample. The purging device (Figure 1) was charged with 5.0 ml of an aqueous solution containing methylene chloride, chloroform, benzene, and 2-butanone, each in excess of 10 mg/l. As this solution was being purged with nitrogen, 3 µl aliquots were periodically withdrawn for analysis by direct aqueous injection. Analyses were performed on the aqueous mixture until the concentrations of the dosed materials were reduced to or below the limit of detection, approximately 100 µg/l. This experiment was

initially performed with a purge gas flow rate of 20 ml/min nitrogen. The flow rate was reduced 65% to 13 ml/min and the experiment repeated. The percent of the dosed compounds remaining in the aqueous phase with respect to the purge volume are listed in Table I.

TABLE I. PURGING OF SELECTED COMPOUNDS FROM WATER

Nitrogen purge gas		Percent remaining in aqueous phase			
Flow rate, ml/min	volume, ml	Methylene chloride	Chloroform	Benzene	2-Butanone
20	0	100	100	100	100
20	20	60	55	46	95
20	100	0	0	3	96
20	300	0	0	0	80
13	0	100	100	100	100
13	6.5	67	94	71	100
13	85	30	29	6	86
13	143	6	0	0	74
		Solubility in water, %			
		2	1	0.08	35
		Boiling point, °C			
		40.1	61.3	80.1	79.6

Those trap saturation volumes reported in Table II and designated by footnote b were obtained by Bellar and Sigsby (9) for a dry air system. To determine what effect, if any, water which is inherent to the system reported here, would have on the saturation volumes, we redetermined them using water saturated nitrogen as the purge gas. Little or no change was observed. The saturation volumes for several organochlorine compounds, not previously reported, were also determined under this condition.

The purging and trapping system was tested with selected industrial solvents over a wide range of concentrations. Ideally, the response for each compound would be linear over the entire concentration range. With the use of the standard solutions and operating parameters described above, the data listed in Tables III through VI were obtained. The peak height of each compound was measured and divided by the concentration to give the slope between zero/zero and each data point collected. Response curves for four common organic solvents are shown in Figure 5. The standard deviations from the mean slope are also listed in the Tables.

TABLE II. TRAP SATURATION VOLUMES, ml

Compound	Silica gel layer	Pora Pak Q	Chromo-sorb	Tenax GC	Retention index
Methane	<5[a]	<5[a]	<5[a]	d	100
Ethane	<25[a]	<5[a]	<5[a]	d	200
Propane	>50[a]	<50[a]	<10[a]	d	300
n-Butane	>500[a]	<100[a]	<20[a]	d	400
n-Pentane	>500[a]	<250[b]	<50[b]	d	500
n-Hexane	>500[a]	>500[b]	>500[b]	>500[b]	600
n-Alkanes C_7 to C_{15}	d	>500[b]	>500[b]	>500[b]	700 - 1500
Benzene	>500[a]	>500[b]	>500[b]	>500[b]	--
Toulene	>500[a]	>500[b]	>500[b]	>500[b]	--
Methylene chloride	d	>500[c]	>500[c]	>500[c]	--
Chloroform	d	>500[c]	>500[c]	>500[c]	--
Aldehydes C_2 & above	Nonquanti-tative	>500[a]	>500[a]	d	--
Phenols	d	>500[a]	>500[a]	d	--
Naphthylene	d	>500[a]	>500[a]	d	--
Chlorobenzene	d	d	>500[c]	>500[c]	--
o-Dichlorobenzene	d	d	>500[c]	>500[c]	--
1,2,4-Trichloro-benzene	d	d	>500[c]	>500[c]	--

[a]Values reported by Bellar and Sigsby (9), 1970.

[b]Values determined using water-saturated nitrogen as purge gas are same as those reported under dry conditions [Bellar and Sigsby (9), 1970].

[c]Determined for this study.

[d]Not determined.

TABLE III. SYSTEM RESPONSE TO METHYLENE CHLORIDE

Concentration, µg/l	Slope 0,0 to data point		Dilution
5.2	78.5		1/100
10.4	76.9		2/100
20.8	78.5		5/100
52.0	77.5		10/100
104.0	76.3		20/100
260.0	72.9		50/100
520.0	85.7		Stock solution
	78.0	Mean	
	3.88	Standard deviation	

TABLE IV. SYSTEM RESPONSE TO CHLOROFORM

Concentration, µg/l	Slope 0,0 to data point		Dilution
6.2	32.3		1/100
12.4	29.7		2/100
24.8	28.1		5/100
62.0	26.8		10/100
124.0	26.8		20/100
310	25.4		50/100
620	29.9		Stock solution
	28.4	Mean	
	2.35	Standard deviation	

TABLE V. SYSTEM RESPONSE TO BENZENE

Concentration, µg/l	Slope 0,0 to data point	Dilution
3.5	220.6	1/100
7.0	219.4	2/100
14.0	214.9	5/100
35.0	215.8	10/100
70.0	207.5	20/100
175.	196.0	50/100
350.	232.0	Stock solution
	215.2 Mean	
	11.4 Standard deviation	

TABLE VI. SYSTEM RESPONSE TO TOLUENE

Concentration, µg/l	Slope 0,0 to data point	Dilution
3.5	120.	1/100
7.0	120.	2/100
14.0	116.	5/100
35.0	115	10/100
70.0	111.	20/100
175.0	105	50/100
350.0	124	Stock solution
	116. Mean	
	6.27 Standard deviation	

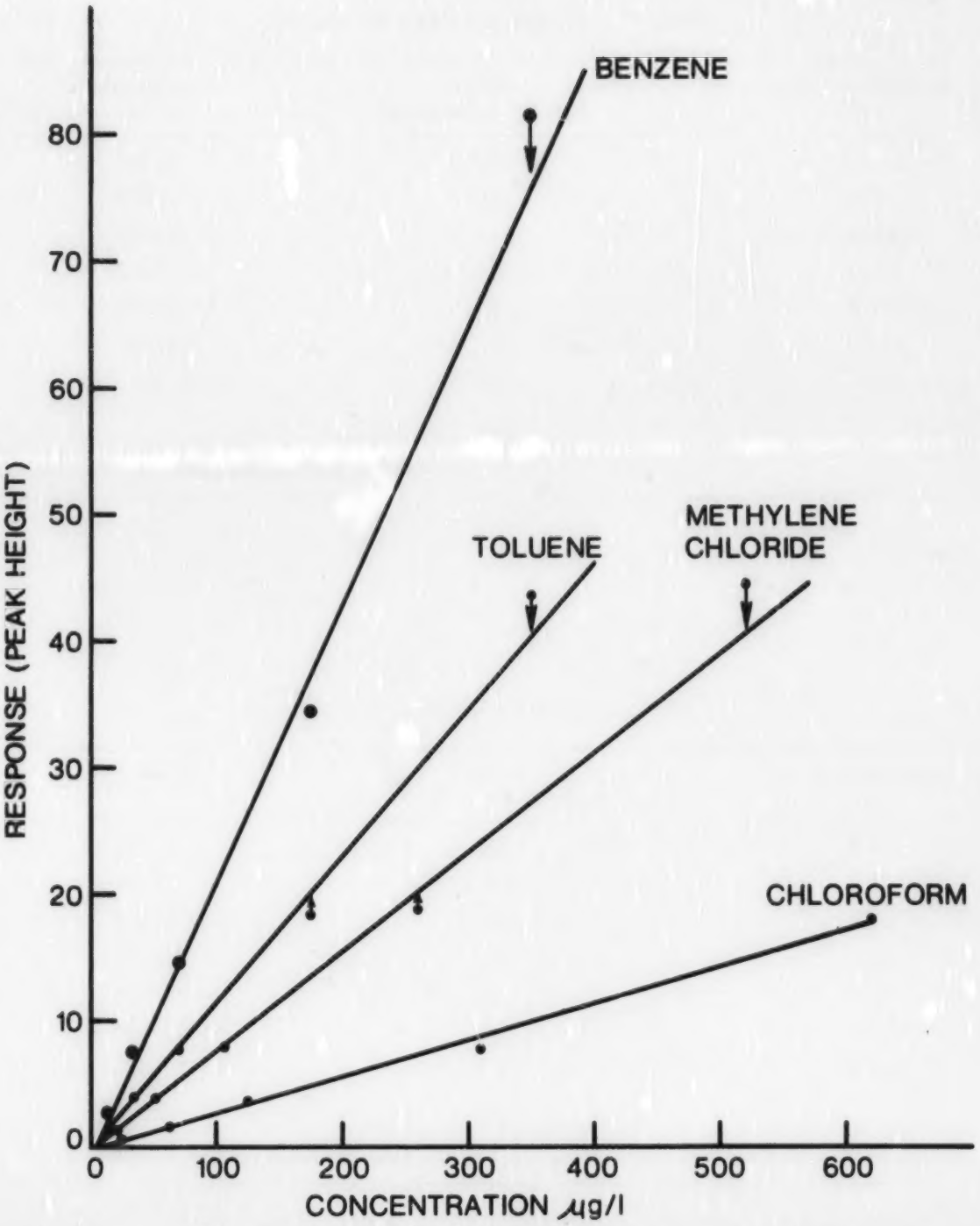

FIGURE 5 RESPONSE CURVES FOR SELECTED ORGANIC COMPOUNDS

To determine the effect of variation in the physical properties of individual compounds on the efficiency of the system, a homologous series of n-alkanes was tested. The test mixture consisted of n-C_5 to n-C_{15} in organic-free water. This mixture was analyzed according to the prescribed procedure using a Tenax trap. Tenax was used as the adsorbent because it has a higher thermal stability than Chromosorb 103 and could be operated at the temperatures required for desorbing the higher molecular weight alkanes. To determine the purge volume required for quantitative transfer of hydrocarbons over the wide boiling range, successive fractions were collected at ambient temperature (19.5°C) and analyzed by flame ionization (FID) gas chromatography using an SE-30 column (see Table VII). The test was repeated at an elevated purging temperature (65°C) (Table VIII).

TABLE VII. PURGING EFFICIENCY AT 19.5°C, % RECOVERY

Purge volume, ml N_2	Compound and boiling point							
	n-C_5 (36°C)	n-C_6 (69°C)	n-C_7 (98°C)	n-C_8 (126°C)	n-C_9 (150°C)	n-C_{11} (196°C)	n-C_{13}[a] (234°C)	n-C_{15}[a] (270°C)
0-60	100	100	98	90	76	60	44	2
60-120			2	6	12	15	17	13
120-240				3	8	9	13	27
240-360				1	3	4	6	14
360-480					1	2	3	8
480-600						2	5	7
600-720						2	3	5
720-840						1	2	5
840-960						1	2	4
960-1080						1	2	4
1080-1200						2	2	7

[a]Not 100% purged using 1560 ml N.

TABLE VIII. PURGING EFFICIENCY AT 65°C, % RECOVERY

Purge volume, ml N_2	Compound and boiling point							
	n-C_5 (36°C)	n-C_6 (69°C)	n-C_7 (98°C)	n-C_8 (126°C)	n-C_9 (150°C)	n-C_{11} (196°C)	n-C_{13}[a] (234°C)	n-C_{15}[a] (270°C)
0-60	100	100	100	100	97	76	66	27
60-120					3	10	12	24
120-240						6	6	15
240-360						4	6	11
360-480						2	4	7
480-600						1	3	6
600-720						1	2	6
720-840							1	4

[a]Not 100% purged.

When the method was applied to a sample from a local sewage plant that serves a diverse industrial area, the complicated FID gas chromatogram shown in Figure 6 resulted. The sample was analyzed again using the microcoulometric detector which gave the chromatogram shown in Figure 7. The compounds identified in the chromatograms were confirmed by GC-MS.

RESULTS AND DISCUSSION

The data in Table I show that it is possible to purge the water insoluble (<2% soluble) compounds from 5 ml of water using less than 150 ml of nitrogen. Decreasing the purge gas flow rate by 65% showed that a slight increase in the volume of purge gas is needed for quantitative transfer. Water-soluble materials whose partition coefficients do not favor the gaseous phase are only qualitatively transferred regardless of the purge volume.

Trapping

From the data reported by Bellar and Sigsby (9) and other data exhibited in Table II, it can be seen that organics contained in small volumes of water saturated nitrogen can be concentrated. It is apparent from these data that compounds with a retention index greater than 500 can be quantitatively purged and trapped. Retention indices given in the literature on porous polymers (11-13) make it possible to predict trap saturation volumes for a wide variety of organic compounds. Since most hydrocarbons and substituted hydrocarbons commonly present in waste waters have retention indices >500, porous polymers were used in developing this method.

Water has a retention index of less than 300 and is not quantitatively trapped by porous polymers. Therefore, gas chromatographic columns and detectors adversely affected by water can be used with a minimum of interference.

The statistical data generated in Tables III through VI reflect an accumulation of errors for the entire method. Considering the number of manipulations involved and that gas chromatographic errors are generally ±3%, it appears that this is, indeed, a useful method. Further study of these data indicates that the majority of the errors are due to the volumetric dilution procedure. The larger the pipet used to withdraw aliquots of the stock solution, the larger the error. A buret may be a more suitable device for delivering volatile solutes.

From the data in Table I and for the compounds studied, we estimated that purging transferred at least 99% of the volatile, water-insoluble compounds from the aqueous phase to the gaseous phase. The data in Tables III through VI and some unreported duplicate data show that the purging efficiency is identical from 2,500 µg/l to at least 6 µg/l. Therefore, the compounds studied can be quantitatively determined over that concentration range.

From the data listed in Table VII it is also apparent that the alkanes up to C_9 can be quantitatively purged using less than 500 ml of purge gas.

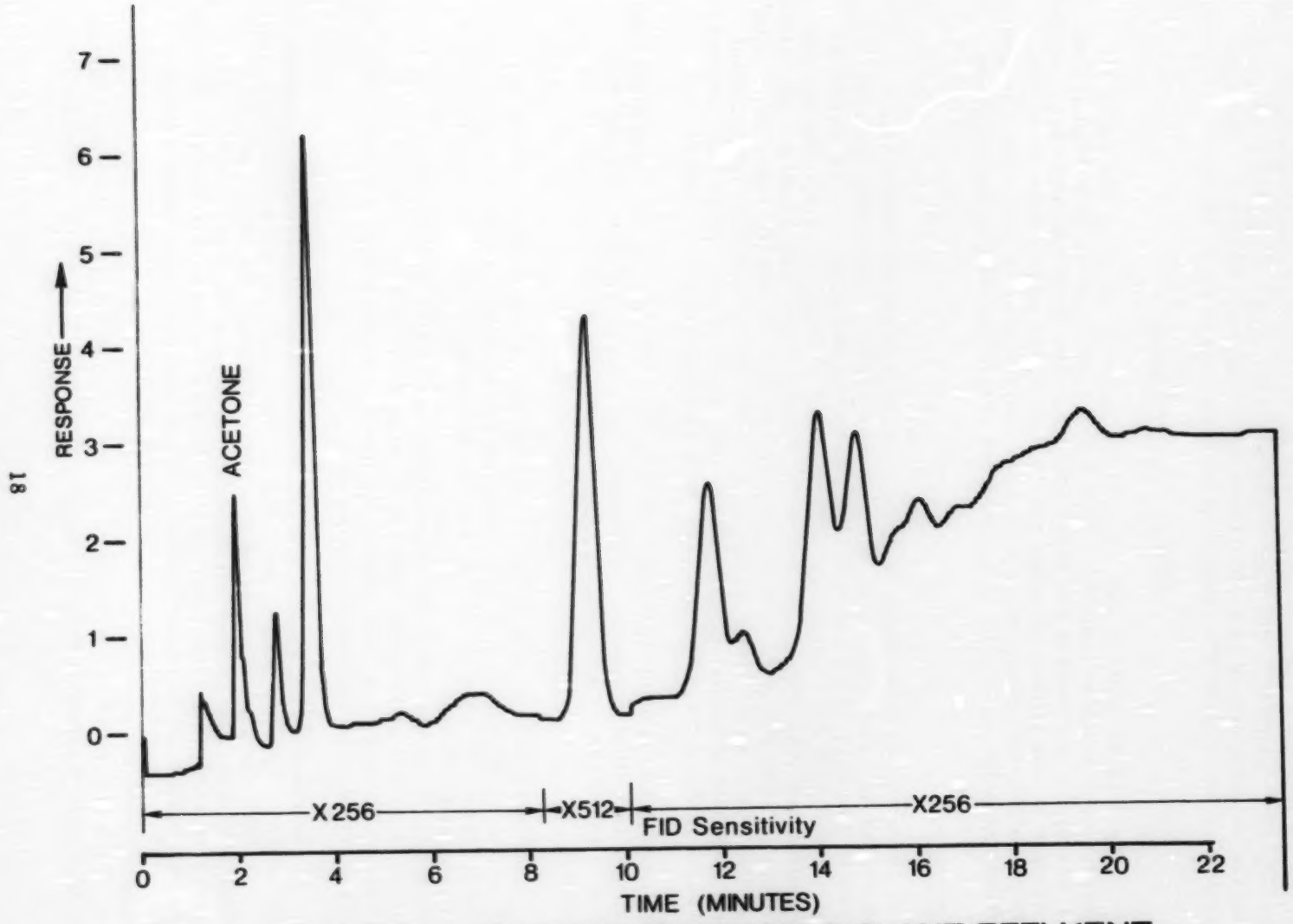

FIGURE 6. SEWAGE TREATMENT PLANT EFFLUENT

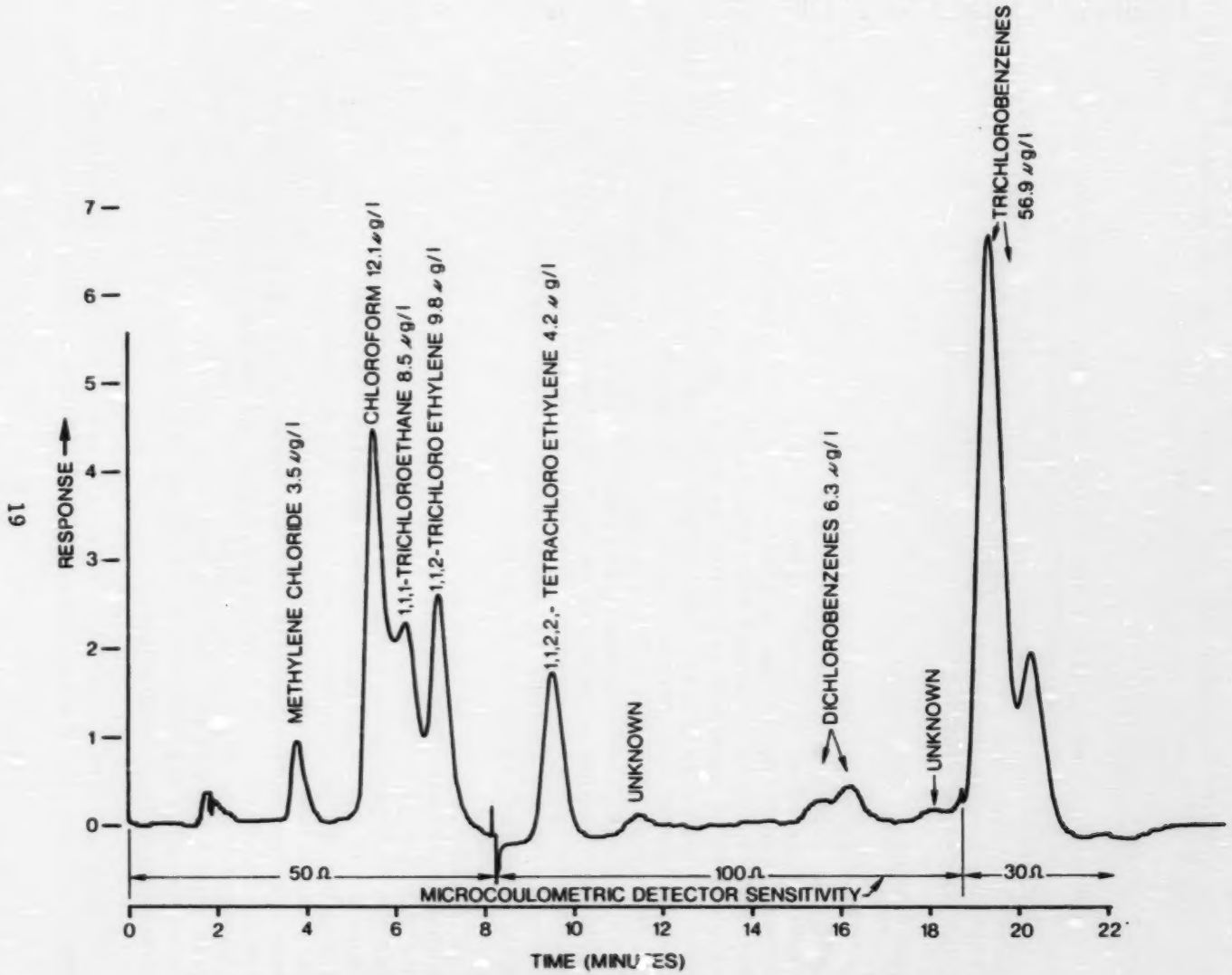

FIGURE 7 SEWAGE TREATMENT PLANT EFFLUENT

Purge volumes exceeding 1.5 l failed to transfer 100% of the C_{11} through C_{15} alkanes. Raising the temperature of the purging device and sample (Table VIII) extended the useful range of the method to C_{11} hydrocarbons. If a water sample contains volatiles over the entire boiling range represented by these data, it may be necessary to trap two fractions in order to perform a complete quantitative analyses on the sample. This is apparent from the data in Table II; they show that compounds with a retention index of less than 600 will saturate the trap and be vented before the high boiling materials are quantitatively purged.

Sample preservation

Due to the volatility of the organic materials detected by this method, common sample preservation techniques are inadequate (3,4). The simplicity of the trap and purging device makes it possible, however, to collect, purge, and trap the sample at the sampling site. The trap and contents can then be sealed and shipped to the laboratory for analysis, and the need for sample preservation is, thus, eliminated.

Application of the method

From the experimental data reported in this paper, it is apparent that this method has great potential for the analysis of trace volatile organics contained in a wide variety of water sources. For quantitative determinations, the method is limited to organic compounds that are less than 2% soluble in water and that boil below 200°C. Significant qualitative enhancement of compounds whose boiling points exceed 200°C can be expected when the sample is heated. The method is useful from 1 to 2,500 µg/l with the use of most gas chromatographs. At concentrations exceeding 2,500 µg/l, chromatograph column flooding and nonlinear detector responses generally occur. Since direct aqueous injection techniques are useful down to 1,000 µg/l the two methods can be used together to perform analyses over a wide range of concentrations. For water soluble compounds, the distillation technique should provide the supplemental methodology needed to analyze most industrial effluents and natural waters.

A wide variety of waste water samples have been analyzed using the method described. The chromatograms (Figures 6 and 7) show the results of one such analysis. Qualitative identifications were made using desorber #2 and the Finnigan GC-MS system. The quantitative analyses were obtained using Desorber #1 with a microcoulometric detector. Only one of the peaks in the FID chromatogram have been identified. At the sensitivity ranges shown, only the chlorobenzenes are likely to appear on the FID chromatogram. The method worked well except for the following: One sample collected from a sewage treatment plant foamed excessively and caused liquid water to be transported from the purging device into the trap. Decreasing the sample size from 5 to 3 ml or using the foam trap eliminated this problem. Liquid water entering the trap causes nonquantitative trapping and severe gas chromatographic interferences.

When only water-insoluble materials were detected in the sample, it was found that the purged water could be withdrawn with a syringe and the

purging device could be recharged for successive analyses without cleaning. When gross amounts of water soluble organics were present, a sufficient quantity of these compounds was collected in the trap for qualitative identification. When this occurred it was necessary to dry the purging device in an oven at 110°C before an interference-free successive analysis could be performed. Other researchers (14,15) have reported on similar methods for the analysis of aqueous samples; their work has been primarily qualitative. This present work has shown that the method can be used for the quantitative measurement of a wide variety of water-insoluble compounds whose boiling points are less than 150°C. By slightly modifying the method, materials that boil at approximately 200°C can also be quantitatively measured. Qualitative sample concentration occurs for a wide variety of other materials for which quantitative measurements could possibly be made if recovery factors were experimentally determined. Vinyl chloride is one compound of considerable current interest that can be determined by this method. Analytical conditions for this specific application are under investigation.

REFERENCES

1. "National Pollutant Discharge Elimination System, Proposed Forms and Guidelines for Information from Owners and Operators of Point Sources," Federal Register, 38 (75, Part II), 9783, Apr. 19, 1973.

2. "Ocean Dumping Criteria," Federal Register, 38 (94, Part II), 12872, May 16, 1973.

3. Sugar, J.W., Conway, R.A., "Gas-Liquid Chromatographic Techniques for Petrochemical Wastewater Analysis," J.W.P.C.F., 40, 1622 (1968).

4. ASTM D 2908-70T, "Tentative Recommended Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography," Annual Book of ASTM Standards, Part 23, Water; Atmospheric Analysis (1973).

5. "Methods for Organic Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio (1971).

6. Dudenbostel, B.F., "Method for Obtaining GC/MS Data of Volatile Organics in Water Samples," Internal Report, U.S. Environmental Protection Agency, Region II, Edison, New Jersey, May 14, 1973.

7. "Procedure for Water Soluble Volatile Organic Solvent in Effluents and Streams," Organic Laboratory, Chemical Services Branch, Region IV, U.S. Environmental Protection Agency, Athens, Georgia, Aug. 1973.

8. "Chlorinated Organics and Hydrocarbons in Water by Vapor Phase Partitioning and Gas Chromatographic Analysis," Method No. QA-466, Dow Chemical, Louisiana Division, Plaquemine, Louisiana, Jan. 1972.

9. Bellar, T.A., Sigsby, J.E., "Non-Cryogenic Trapping Techniques for Gas Chromatography," Internal Report, Reprints available from: John E. Sigsby, Jr., Division of Chemistry and Physics, U.S. Environmental Protection Agency, Research Triangle Park, N.C. (1970).

10. Bellar, T.A., Sigsby, J.E., "The Analysis of Light Aromatic Carbonyls, Phenols, and Methyl Naphthylenes in Automotive Emissions by Gas Chromatography," Internal Report, Reprints available from: John E. Sigsby, Jr., Division of Chemistry and Physics, U.S. Environmental Protection Agency, Research Triangle Park, N.C. (1970).

11. Chromosorb Century Series Bulletin, Johns-Manville, Celite Division, Greenwood Plaza, Denver, Colorado, Nov. 1970.

12. Tenax-GC Bulletin No. 24, Applied Science Laboratories, Inc., P.O. Box 440, State College, Pa.

13. Hollis, O.L., and Hayes, W.V., "Water Analysis by Gas Chromatography Using Porous Polymer Columns," J. Gas Chromatography, 4, 235 (1966).

14. Zlatkis, A. and Liebich, H.M., "Profile of Volatile Metabolites in Human Urine," Clin. Chem., 17, 592 (1971).

15. Novak, J., Zluticky, J., Kubelka, V., Mostecky, J., "Analysis of Organic Constituents Present in Drinking Water," J. Chromatog., 76, 45 (1973).

APPENDIX

LIST OF PARTS AND INSTRUCTIONS FOR ASSEMBLY

OF PURGING DEVICE, TRAP, AND DESORBERS

PURGING DEVICE

The purging device (Figure 1) is constructed from glass tubing. The glass frit installed at the base of the sample reservoir allows finely divided gas bubbles to pass through the aqueous sample while containing the sample above the frit. The sample reservoir is designed to provide maximum bubble contact time and efficient turbulent mixing. Gaseous volumes above the sample reservoir are kept to a minimum to provide efficient transfer characteristics and yet allow sufficient space for most foams to disperse. Inlet and exit ports are constructed from 1/4-in. O.D. medium-or heavy-wall tubing so that leak-free removable connections can be made using "finger tight" compression fittings containing plastic ferrules. The optional foam trap is used to control occasional samples that foam excessively.

Parts for purging device:

Borosilicate Glass tubing - 6 mm O.D. Standard Wall, 14 mm O.D. Standard Wall, and 1/4 in O.D. Medium Wall

10 mm glass frit, medium porosity

6 mm gas chromatographic half-hole septum or septum plugs

5 ml syringe

Syringe valve-Hamilton (1 ELI 2 way)

17 cm x 20 gauge syringe needle

Stainless steel reducing union 1/4 in to 1/8 in with Teflon or nylon ferrules to attach trap to purging device exit.

TRAP

The trap is assembled and packed with the appropriate adsorptive material according to Figure 2. The body assembly acts as a seal for the exit end of the trap. The modified stem assembly is used to attach the trap to the desorption device. The cap is used to seal the inlet end of the trap when it is not in use (finger-tight).

Parts for trap:

Stainless steel tubing 3.175 mm (0.125 in) O.D. x 2.67 mm (0.105 in) I.D. x 21.6 cm long - (trap body)

Body assembly Swagelok quick-connect (QC4-B-200) (the trap vent)

Stem assembly Swagelok quick-connect (QC4-S-200) modified (Drill through with a #30 (0.128 in) drill to allow trap body to pass through entire fitting)

Swagelok cap (200-C with Teflon or nylon ferrules)

DESORBERS

Desorber #1 (Figure 3) is attached directly onto the gas chromatograph liquid inlet system after removing the septum nut, the septum, and the internal injector parts. The modified body assembly is screwed onto the inlet system using the Teflon gasket as a seal. A Swagelok plug (200-P) is attached to one of the stem assemblies. These assembled parts called simply "the plug" are used to seal the desorber whenever the trap is removed to maintain the flow of carrier gas through the gas chromatographic column. The flow controller, Teflon tubing and stem assembly are used to provide the trap backflush flow. This entire assembly is also used to provide gas flow to operate the purging device.

Parts for Desorber #1:

Brooks Model 8744 flow controller with #1 taper needle

Teflon tubing 3.175 mm (0.125 in) O.D. x 1.65 mm (0.065 in) I.D. x 1.5 m (5 ft) long

Stem assembly - 3 each Swagelok (QC4-S-200)

Body assembly Swagelok (QC4-B-2PF) modified with pipe threads drilled out using a 25/32 in drill. The fitting is rethreaded using a 7/16-20 bottoming tap. (The check ball and spring located within the body assembly are removed and discarded.)

Teflon gasket approximately 6.35 mm (1/4 in) thick x 19.8 mm (25/32 in) O.D. x 3.97 mm (5/32 in) I.D.

Swagelok plug (200-P)

Desorber #2 (Figure 4) may be attached to any gas chromatograph by piercing the GC liquid inlet septum with the needle. The desorber is assembled according to Figure 4 with internal volumes and dead volume areas held to a minimum. The heat source is concentrated near the base of the desorber so that the internal seals of the body assembly do not become damaged by heat. The use of a detachable needle assembly from a micro syringe

makes it easy to replace plugged or dulled needles. The flow controller, Teflon tubing, and stem assembly are used to provide the trap backflush flow. This entire assembly is also used to provide gas flow to operate the purging device.

Parts for Desorber #2:

Brooks Model 8744 flow controller with #1 taper needle

Teflon tubing 3.175 mm (0.125 in) O.D. x 1.65 mm (0.065 in) I.D. x 1.5 m (5 ft) long

Stem assembly Swagelok quick-connect (QC-S-200)

Body assembly Swagelok quick-connect (316-QC4-B-400) modified (The check ball and spring are removed and discarded.) A 0.128 in hole is drilled through the hex area of the fitting and the Swagelok reducing adaptor is silver soldered in place. Be sure to remove plastic seals located inside the body assembly fitting before silver soldering.

Stainless steel tubing 6.35 mm (1/4 in) O.D. x 4.763 (3/16 in) I.D. x 13 cm long

Cap - Swagelok (316-400-C)

Reducer - Swagelok (316-100-R-2)

Thermocouple, compatible with pyrometer on gas chromatograph

Heater tape, useful up to 250°C

Asbestos tape

Heat resistent fiber glass tape

Micro syringe needle - 26 gauge x 51 mm (2 in) and detachable syringe needle assembly from micro syringe (Glenco)

Variable transformer, 0 to 140 volts.

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